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STUDIES ON THE RATE OF CATALYTIC HYDROGENATION OF DIPHENYL KETIMINE

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BY

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STUDIES ON THE RATE OF CATALYTIC HYDROGENATION OF DYPHENYL KETIMINE

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To my wife Genevieve for her love, self sacrifice and devotion.

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CHAPTER I

INTRODUCTION

While a great number of kinetic studies have been made on catalytic reductions in the gaseous phase, relatively few liquid phase catalytic hydrogenations have been studied.

A large majority of the liquid phase catalytic hydrogenations are zero order with respect to the concentration of the hydrogen acceptor, and first order with respect to the hydrogen pressure, at least during the early stages of the reduction.

Two general theories have been advanced to try to explain heterogeneous catalytic reactions in general. The Langmuir-Hinshelwood[1,2] theory holds that the reacting molecule or molecules will all be adsorbed by the catalyst. An activated complex is then formed between the reacting molecule(s) and the catalyst. This in turn forms the reaction products, which are more or less rapidly desorbed by the catalyst, depending on their attraction to it. This theory is believed to apply in most catalytic reactions. It is flexible enough to explain most experimental data.

The Rideal-Eley[3] theory holds that only one of the reacting molecules is adsorbed by the catalyst. The adsorbed molecule in turn

reacts with another molecule in the gas or liquid phase, or in a van der Waals' layer to form an activated complex which again involves the catalyst. This activated complex then gives the reaction products which are subsequently desorbed by the catalyst. This theory is believed to hold in some catalytic reactions; particularly, the hydrogenation of the nitro group in nitrobenzene, using a platinum catalyst, with acetic acid as solvent, takes place by a Rideal-Eley mechanism.[4]

Liquid phase catalytic hydrogenations the kinetics of which have been studied include a variety of types of hydrogen acceptors, solvents, catalysts and conditions. In the following discussion, liquid phase hydrogenations upon which kinetic studies have been made are catalogued under type of hydrogen acceptor. All of the following reductions were found to be zero order with respect to the hydrogen acceptor, except where specifically stated to the contrary.

Hydrogenation of Aromatic Nuclei. Rate studies have been made on the hydrogenation of the aromatic nuclei in benzene, alkyl benzenes, phenyl substituted aliphatic acids, phenols, aromatic amines, and of naphthalene and 1-naphthol;

Examples include benzene with Ni,Cr[5], with Pd black[6], Pt[7], Pd on silica gel[8] catalysts; the benzene ring in various phenyl substituted aliphatic acids using Pt catalyst[9];

Various phenols using Ni catalyst[10], and with Pt catalyst[7];

Aniline with Pt catalyst[11], and various aromatic amines with Ni catalyst[10];

Naphthalene on Pt[10], 1-naphthol on Ni[7] and biphenyl on Ni,Cr catalyst[5].

Hydrogenation of Olefinic, Acetylenic and Carbonyl Compounds. Rate studies on the reduction of olefinic compounds comprise a majority of such studies in the liquid phase. Examples include vegetable and animal oils using Ni[12], oleic acid with Pt[13], and with Pt,$BaSO_4$[14] catalysts; oleyl alcohol on Pt black[15]; 25 straight chain olefinic acids and esters using Pt, Ni and Co[16]; crotonic acid with Pt[17] and with Ni[18]; styrene with Pt on $BaSO_4$[19], with Ni[20,21]; several vinyl ethers over Pd,$CaCO_3$[22]; dimethylvinylcarbinol with Ni[23]; cinnamyl alcohol using Ni[24]; methyl cinnamate over Ni[25] and sodium cinnamate with Pd[26] and Ni[27]; allyl alcohol using Ni[4, 10, 28], Co[29], Pt[33, 34] and Ru, Rh and Pd catalysts[32]. Hexene-1 with Ni[29], Ru[32], Rh[32], Pd[32], and Pt[33,34]; various terpenes with Pt catalyst[35];

Methylethylethynylcarbinol using Ni[36]; Dimethylethynylcarbinol with Ni[37]; sodium propiolate with a Pd sol catalyst[26]; the carbon to oxygen double bond in various ketones and aldehydes with Ni catalyst[28].

Cinnamic acid on Ni[38] was found to be first order with respect to cinnamic acid.

Nitrogen Compounds. Nitro groups of nitrobenzene and 1-nitro naphthalene using Ru, Rh and Pd catalysts[32], and of nitrobenzene with Pt[11]. The oxime of 3-phenyl-2-ketopropionic acid over Pd, charcoal catalyst[39]. All obeyed zero order kinetics.

Nitromethane[11], and various azines[40] using Pt catalysts showed first order kinetics with respect to the hydrogen acceptor.

To summarize, the great majority of catalytic hydrogenations in the liquid phase are zero order with respect to the concentration of the hydrogen acceptor, and first order with respect to the hydrogen pressure.

This is apparently true regardless of the catalyst used, if it is true for any catalyst. It should be pointed out that many of the reductions that are zero order initially are inhibited by the reaction products, so that the order of a reaction may change after an appreciable quantity of products has been formed.

Temperature, of course, affects the rate of catalytic hydrogenations. In some cases, changes in the order of the reaction are noted with change in temperature. Maxted and Moon[17] report that the hydrogenation of crotonic acid in acetic acid solution is zero order at 19.4°C, but at 80-90°C the reaction is essentially first order, both at a constant hydrogen pressure. This they explain by the fact that the adsorption of the acid by the catalyst is much less at the higher temperature, thus making diffusion of the acid to the catalyst surface a rate determining factor.

Rate and type of agitation of the reaction mixture has an effect on the rate of catalytic reactions, and sometimes on the order of the reaction also. Watt and Walling[34] found that shaking the hydrogenation vessel at 180 osc/min. gave higher rates than magnetic stirring at 930 rpm. Rideal[26] found the rate of hydrogenation of sodium cinnamate to be proportional to the square of the shaking speed. Goldanskii and Elovich[14] found the rate of hydrogenation of oleic acid to be controlled by diffusion, and thus to approach first order at rates of shaking below 600 osc/min; and to be zero order above 600 osc/min.

The amount of catalyst used has an effect on hydrogenation rates in most cases. As more catalyst is used, the rate generally increases at first, then levels off, sometimes decreasing slightly with further addition

of catalyst. Sokol'skii and Fashman[23] report that with small amounts of Ni catalyst the reduction of dimethylethynylcarbinol is zero order, but with larger amounts of catalyst the rate approximates first order, both at a constant hydrogen pressure.

The type of solvent used may also have a large effect on catalytic hydrogenations. Truffalt[5] reports that benzene would not reduce in acetic acid or acetic annhydride solution with a Ni,Cr catalyst, but would reduce quite well in cyclohexane or hexane solution.

A number of new ketimines have been prepared in the last eight years by Pickard and his co-workers[41-48]. One of the methods used to identify these new compounds was hydrogenation to the corresponding amine. With few exceptions[45-46], the ketimines hydrogenated readily at atmospheric pressure and room temperature. An ethanol solution of the ketimine was used with Adams[49] platinum catalyst.

Relative reduction rates for a series of ditolyl ketimines were determined by Pickard and Vaughan[41]. Their results indicated that ortho substituted ketimines hydrogenated more slowly than did the meta or para substituted compounds.

The relative reduction rate of dialkyl ketimines was found to decrease with increasing size of the alkyl group[45].

For a series of alkyl, ortho tolyl ketimines, the reduction rates decreased with increased size, and with increased branching of the alkyl group[41].

These relative reduction rates were determined in the apparatus described by Vaughan[48]. All of these relative rates were intended to be qualitative since no careful attempt was made to control temperature,

pressure, stirring rate, concentration of ketimine, or amount of catalyst. Each investigator used a different batch of catalyst, and no comparison was made with the activity of one batch to that of another. Thus the various relative rates could not be directly compared.

The object of the present work was to set up a standard method for determining hydrogenation rates of ketimines, and to study the effect of varying the concentration of the ketimine, temperature, agitation rate and the amount of catalyst in the hydrogenation of diphenyl ketimine.

CHAPTER II

EXPERIMENTAL

Materials Used. The diphenyl ketimine used in this research was prepared by the method of Tolbert[50]. Benzhydryl amine was prepared as described below. Tank hydrogen was used as supplied by the National Cylinder Gas Company, without further purification. Absolute ethanol was used as supplied by the U. S. Industrial Chemical Company. All other chemicals were the best grade available, used without further purification.

Preparation of Benzhydryl Amine. Benzhydryl amine was prepared by hydrogenation of diphenyl ketimine using absolute ethanol as a solvent, and Vandenheuvel's catalyst (PS 14)[51]. Two grams of the catalyst in 50 ml. absolute ethanol was prehydrogenated in a Parr type low pressure hydrogenation apparatus. The initial hydrogen pressure was 50 p.s.i.a. Then 18 g (0.1 mole) of diphenyl ketimine in 200 ml. absolute ethanol was added. The rate of hydrogen uptake was rapid at first, but decreased after about an hour. After eight hours about 90% of the theoretical amount of hydrogen was taken up. The product was isolated by filtering the catalyst on a Buchner funnel and distilling the ethanol from the filtrate. The resultant liquid, which was the amine plus a small amount of unreacted imine, was refluxed with concentrated hydrochloric acid for two hours to hydrolyze the imine to benzophenone. The benzophenone was removed by extract-

ion with ether, the aqueous solution was made basic with NaOH solution, and the amine extracted with ether. The ether extract was dried overnight with anhydrous Na_2SO_4, and the ether removed by distillation. The amine so obtained formed an acetate salt upon treatment with glacial acetic acid, m.p. 141°C, reported[52] as 141°, n_D^{20}, 1.5960, reported $n_D^{21.5}$, 1.5963[53].

Apparatus. Apparatus similar to that described by Vaughan[48] was first tried. Very unsatisfactory results were obtained, primarily because of the lack of pressure control. Thus an apparatus in which the pressure could be controlled was necessary. A diagram of the apparatus used for all of the successful experiments is shown in Figure 1. This apparatus was constructed in this laboratory and was adapted from the design suggested by Vandenheuvel[54].

In the following discussion, numbers in parentheses refer to corresponding numbers in Figure 1. The jacketed burette(7), jacketed levelling tube and the differential manometer(15) were mounted on a board about 2' x 4'. Holes were drilled directly behind all the stopcocks, and for the sidearms on the jackets. The burette and levelling tube were held in place by brass bands. All the stopcocks in the apparatus were fitted with pressure retainers.

The hydrogenation flask(14) was made by sealing a ground glass joint on a 25 ml. Erlenmeyer Flask. The flask was dented in four places equally spaced around the wall. The dents were about 1/2 inch deep, and were about one inch above the bottom of the flask. The purpose of the dents was to break up the surface of the liquid in the flask as it was agitated.

HYDROGENATION APPARATUS

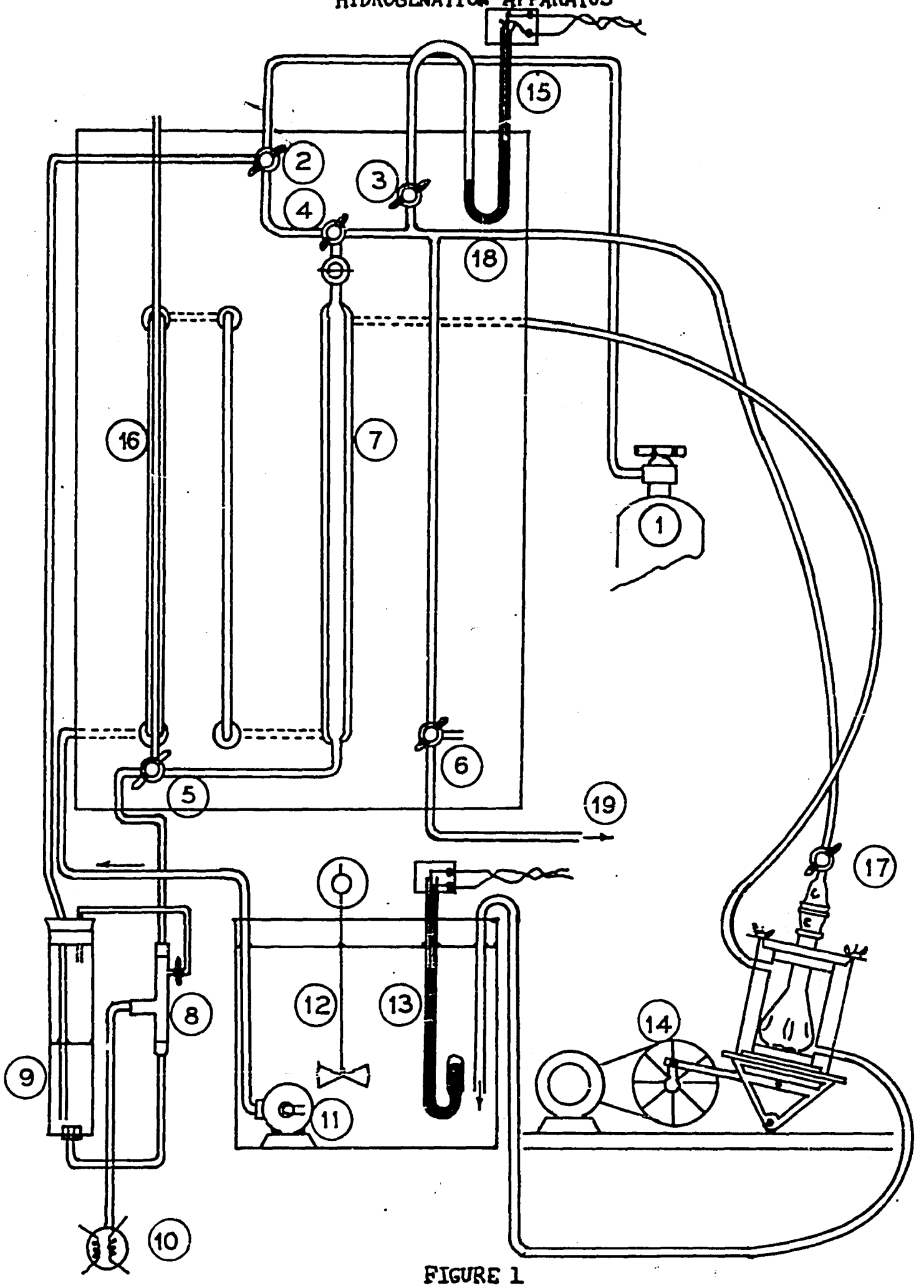

FIGURE 1

The hydrogenation flask was jacketed, and water from a constant temperature bath was circulated through the jackets of the burette, levelling tube and reaction flask by means of a pump(11).

The reservoir(9) of the pump(10) was filled with 95% ethanol, which was used as the hydrogen confining fluid as suggested by Vandenheuvel[54]. The pump(10) was an adjustable bellows type, manufactured by the Precision Scientific Company, Chicago, Illinois. By adjusting the bellows, the amount of liquid delivered by each stroke of the pump could be varied continuously from 0-1 ml.

Constant pressure, within $\pm$ 0.1 mm. of mercury, as measured by a cathetometer, was maintained in the system in the following manner. The differential manometer(15) was about half filled with mercury. A slight lowering of the pressure within the system such as would be caused by hydrogen adsorption, causes the mercury level in the right hand branch of the manometer to lower, breaking contact of the mercury with the upper wire of a two wire switch. This, through a relay, turns on the pump(10) which pumps ethanol into the system, thus increasing the pressure. When the operating pressure is restored, mercury contacts the upper wire, stopping the pump.

The outside of the hydrogenation flask was fitted with a large rubber stopper machined to fit tightly into the jacket, thus making the assembly water tight, and enabling the flask to be removed from the jacket for cleaning. After each use, the flask was cleaned with chromic acid-sulfuric acid cleaning solution. When magnetic stirring was used to agitate the contents of the flask, a regular condenser clamp was used to support the flask and jacket, and another to keep the stopper in. When

shaking was used, the flask and jacket were held in the shaker by means of a collar which fits over the rubber stopper, and was fastened to the shaker by means of wing nuts.

The ground glass joint which closed the hydrogenation flask was connected to the glass tube(18) by means of a piece of flexible "Tygon" tubing. It was found that, as supplied, this tubing was quite permeable to hydrogen. Soaking the tubing for six to eight hours in chloroform eliminated the hydrogen permeability almost completely but, at the same time, hardened the tubing considerably.

The shaker(14) used on the hydrogenation apparatus was of the type used in the Parr low pressure hydrogenation apparatus. It shook the flask through an angle of about 25°. The shaking rate could be varied continuously from 0 - 300 osc/min. by means of a variable transformer. With magnetic stirring for agitation, the speed of stirring was as rapid as possible. The rate of stirring was difficult to control because of the small size of the flask, and could not be determined.

Hydrogenation Rate Determinations. Hydrogenation rates, using the apparatus described above, were determined as follows. A portion of catalyst, weighed by difference to ± 0.1 mg., was added to the hydrogenation flask with a measured amount of solvent. Then the flask was connected to the system. With stopcock(5) closed and stopcock(4) turned so that the burette was closed to the hydrogenation flask, the latter was evacuated for 25 seconds by means of a water aspirator. With valve(1) open, and stopcocks(2) and (4) opened to the hydrogenation flask, the flask was filled with hydrogen. The evacuation and filling of the flask with hydrogen was repeated twice. Timing of the 25 second evacuation period was by

means of a stopwatch.

The burette was then filled with hydrogen by turning stopcock(4) and stopcock(2) into the correct positions. Stopcock(5) was adjusted so that the levelling tube was closed, and the needle valve(8) was opened. This allowed hydrogen to force alcohol from the burette into the reservoir(9). When the burette was filled, stopcocks(3), (4) and (5) were opened to the hydrogenation flask, and stopcock(2) turned so that hydrogen bubbled through the alcohol in the reservoir to keep it saturated with hydrogen. This flow of hydrogen through the reservoir was done continuously, excepting when the hydrogenation flask or burette were being filled.

The pressure in the system was then adjusted to the operating pressure, which was 7.1 mm. greater than the ambient pressure. The adjustment, if the pressure within the system was less than operating pressure, was to turn the pump(10) on. If the pressure was greater than operating pressure, stopcock(16) was opened, and enough hydrogen was let escape so that the pressure fell below operating pressure, then the pump was turned on. The initial volume of hydrogen in the burette was noted and agitation and timing begun. Timing for all the hydrogenation experiments was by means of a spring wound interval timer such as is used in photographic darkrooms. Agitation of the catalyst-solvent system was continued until no more hydrogen was taken up, or for 30 minutes, whichever was longer.

After the catalyst was fully hydrogenated, stopcock(17) was closed, the flask opened, and a measured volume of 0.2408 M diphenyl ketimine in absolute ethanol was added. Then the flask was closed, stopcock(17) opened and the flask again evacuated and refilled with hydrogen three times. The pressure and volume of hydrogen in the burette, were

adjusted as during catalyst hydrogenation. The initial volume of hydrogen was noted, and agitation and timing was begun. Thereafter at convenient intervals of time, usually no shorter than one minute, the volume of hydrogen was read. This was continued until no more hydrogen was taken up. The volume of hydrogen adsorbed in each time interval was reduced to standard conditions. Data on the vapor pressure of the solvents used was taken from Scatchard and Raymond[55]. Plots of kinetic data obtained in this apparatus are shown in figures 2-8.

Determination of the Volume Correction. To determine the volume correction due to the slight diffusion of hydrogen through the flexible tubing, a blank determination was run. This experiment was run exactly as regular in the hydrogenation experiments, except that no catalyst or hydrogen acceptor were added. The results obtained indicated a loss of 0.03 ml. per minute. This correction was made on the data from all the hydrogenations.

Effect of the Amount of Catalyst. Rate studies were made at $35^{\circ} \pm 0.2^{\circ}C$ using 5 ml. ethanol and 5 ml. diphenyl ketimine solution, with shaking at 240 ± 5 osc/min. The amount of catalyst was varied from 8-17 mg. for Adams catalyst, and from 5-52 mg. for PS 14. A plot of the initial rate constant vs. amount of catalyst is shown in Figure 2.

Variation of the Initial Concentration of Diphenyl Ketimine. Using about 25 mg. of PS 14 catalyst at $35^{\circ}C$ with shaking at 240 osc/min., the initial concentration of diphenyl ketimine solution was varied from 2 ml.-8 ml. of 0.2408 M diphenyl ketimine solution in 10 ml. total volume. Results are shown in Figure 3.

Effect of Acetic Acid. The effect of using acetic acid as a

EFFECT OF AMOUNT OF CATALYST

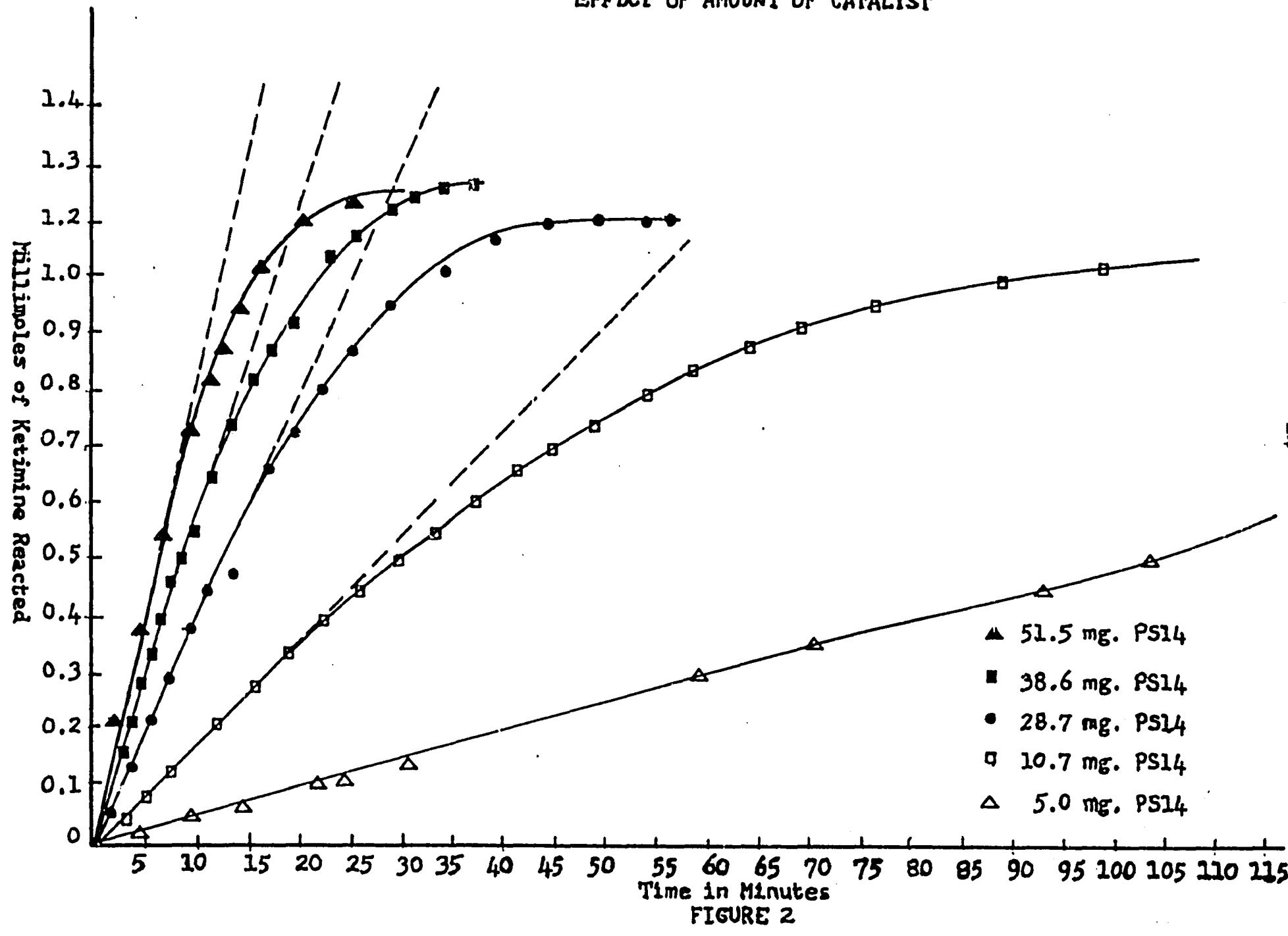

FIGURE 2

solvent, and thus hydrogenating the acetate salt of the ketimine was determined by prehydrogenating the catalyst in 5 ml. of glacial acetic acid, but otherwise using the above described procedure. The catalyst-acetic acid mixture was shaken for 30 minutes after hydrogenation of the catalyst was completed. No volume change, other than that due to hydrogen leakage was noted, indicating that little or no ethyl acetate was formed between ethanol vapors and acetic acid. Five ml. of diphenyl ketimine solution in ethanol was added, and the hydrogenation rate determined as above. About 25 mg. of PS 14 catalyst was used in these runs. Results are shown in Figure 4.

Hydrogenation Rates in Presence of an Excess of Benzhydryl Amine. To determine the effect of an excess of the reduction product on the hydrogenation of diphenyl ketimine, a 25 mg. sample of the catalyst was hydrogenated in a measured sample of diphenyl ketimine solution. This was carried out as in the prehydrogenation of the catalyst described above. About two hours was necessary for the complete hydrogenation of both catalyst and ketimine. Then a measured sample of diphenyl ketimine was added, and the rate of hydrogenation determined as before. Figure 5 is a plot of the results so obtained.

The Effect of Pressure Differences. Using approximately 10 mg. of Adams PtO_2 catalyst, hydrogenation of 5 ml. of diphenyl ketimine solution in ethanol in a total volume of 10 ml. was carried out at an atmospheric pressure of 729.1 mm. and at 743.6 mm. The results indicate a fairly large change with pressure, and show the need for accurate pressure control during the hydrogenation.

Temperature Effect. Hydrogenation rates were determined at 35°,

EFFECT OF INITIAL AMOUNT OF DIPHENYL KETIMINE

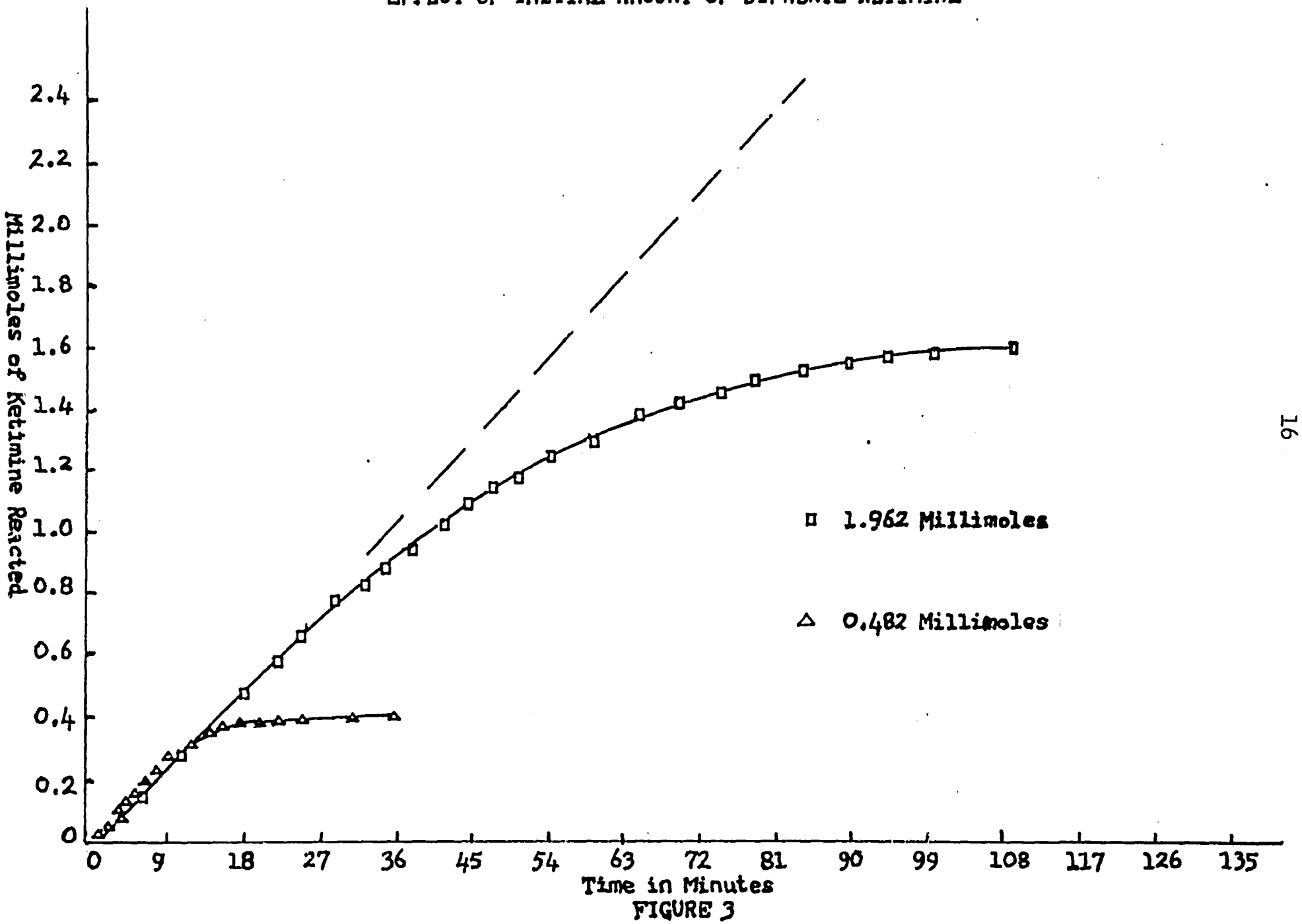

FIGURE 3

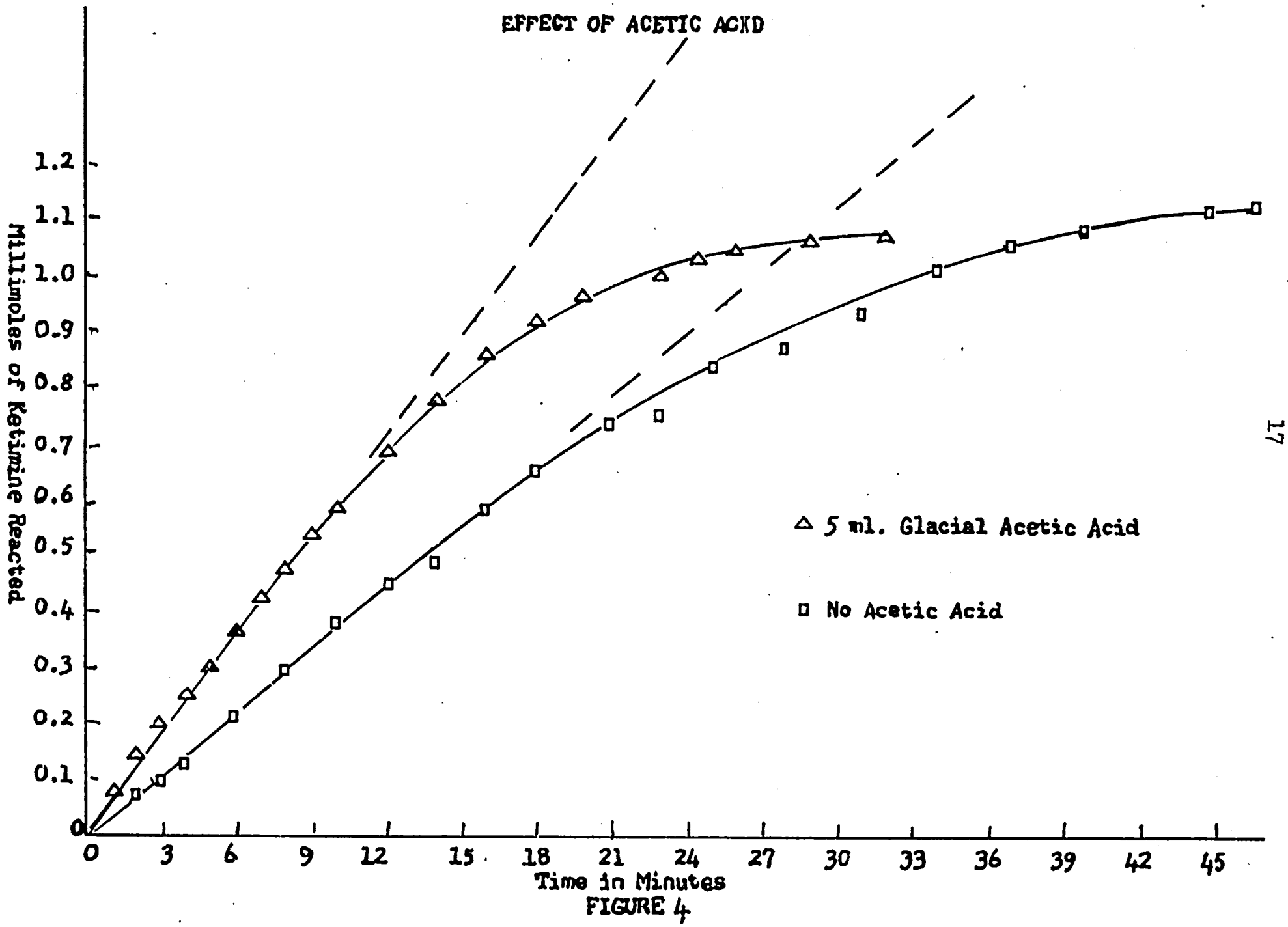
EFFECT OF ACETIC ACID
Millimoles of Ketimine Reacted
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0 3 6 9 12 15 18 21 24 27 30 33 36 39 42 45
Time in Minutes
△ 5 ml. Glacial Acetic Acid
□ No Acetic Acid

FIGURE 4

EFFECT OF AN EXCESS OF PRODUCT

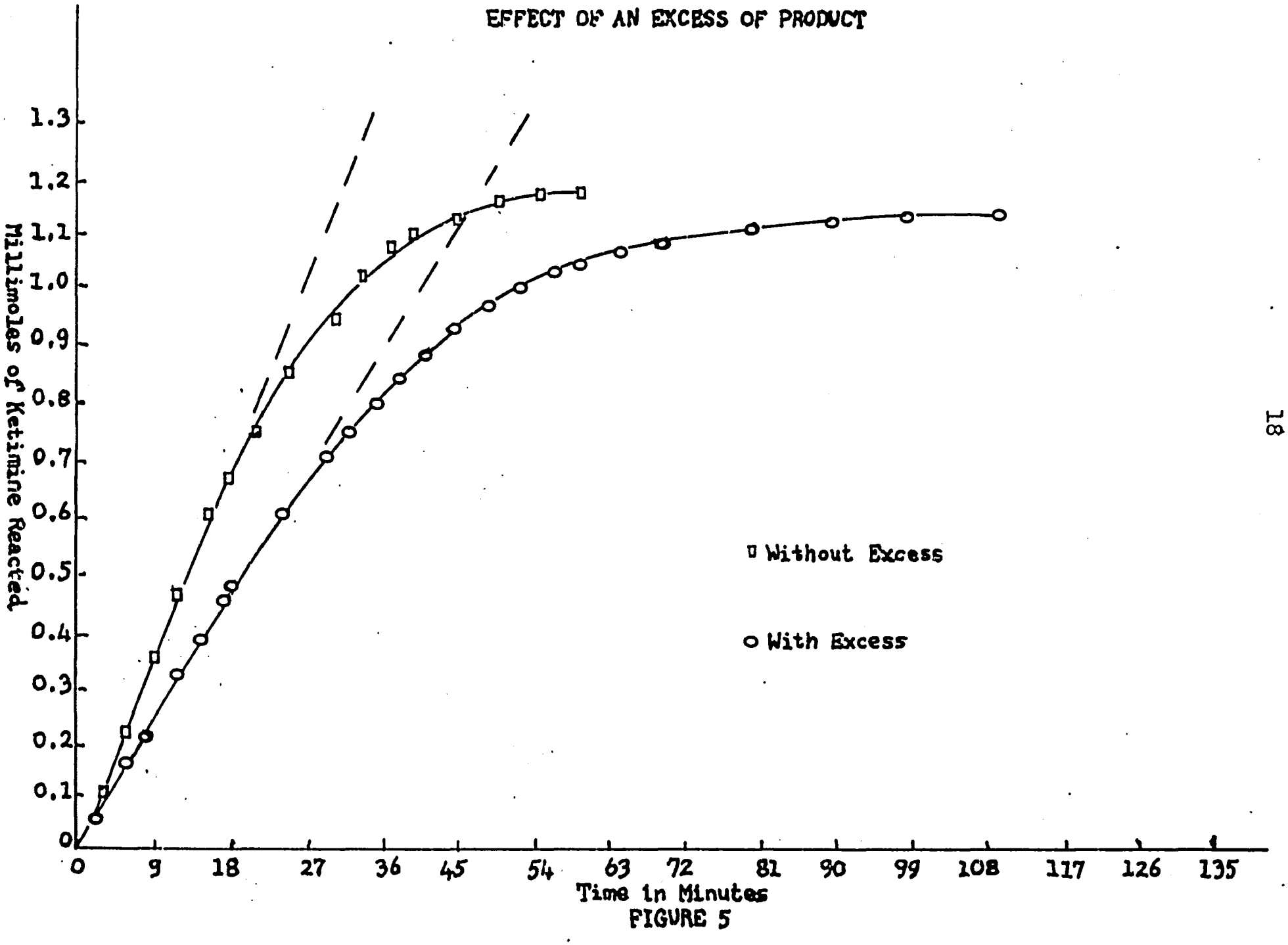

FIGURE 5

40° and 45°C, all temperatures being controlled within 0.2°C. In all cases 25 mg. of PS 14 catalyst was prehydrogenated in 5 ml. absolute ethanol. Then 5 ml. of diphenyl ketimine solution was added, and the rate of hydrogenation determined. The shaking rate was 240 ± 5 osc/min. Results are shown in Figure 7.

Agitation Rate. The effect of variation of the rate of agitation was studied. Five ml. of diphenyl ketimine solution were used in 10 ml. total volume of ethanol. Twenty-five mg. of PS 14 catalyst was used. The temperature was 35 ± 0.2°C. Figure 8 shows hydrogenation data for shaking rates varying from 120-360 osc/min.

Catalyst Poisoning by Anhydrous Hydrogen Chloride. It was found impossible to hydrogenate PS 14 catalyst in the presence of an absolute ethanol solution of anhydrous hydrogen chloride. It was found impossible to hydrogenate diphenyl ketimine hydrochloride on prereduced PS 14 catalyst using ethanol as solvent.

Standardization of Catalysts. For standardization purposes, the rate of hydrogenation of maleic acid was determined on both of the catalysts used. Five ml. of a 0.2395 M solution of Maleic acid in absolute ethanol was added to the prereduced catalyst in five ml. absolute ethanol. Ten mg. of Adam's catalyst and 25 mg. of PS 14 were used in separate runs. The temperature was 35 ± 0.2°C, and the agitation rate was 240 ± 5 osc/min. Figure 9 shows the results obtained.

Many duplicate runs were made that are not shown in the Figures, and checking results were obtained in all cases. Also a great many runs with PtO_2 catalyst are not included because of the fact that they were almost identical with corresponding runs using PS 14.

EFFECT OF PRESSURE

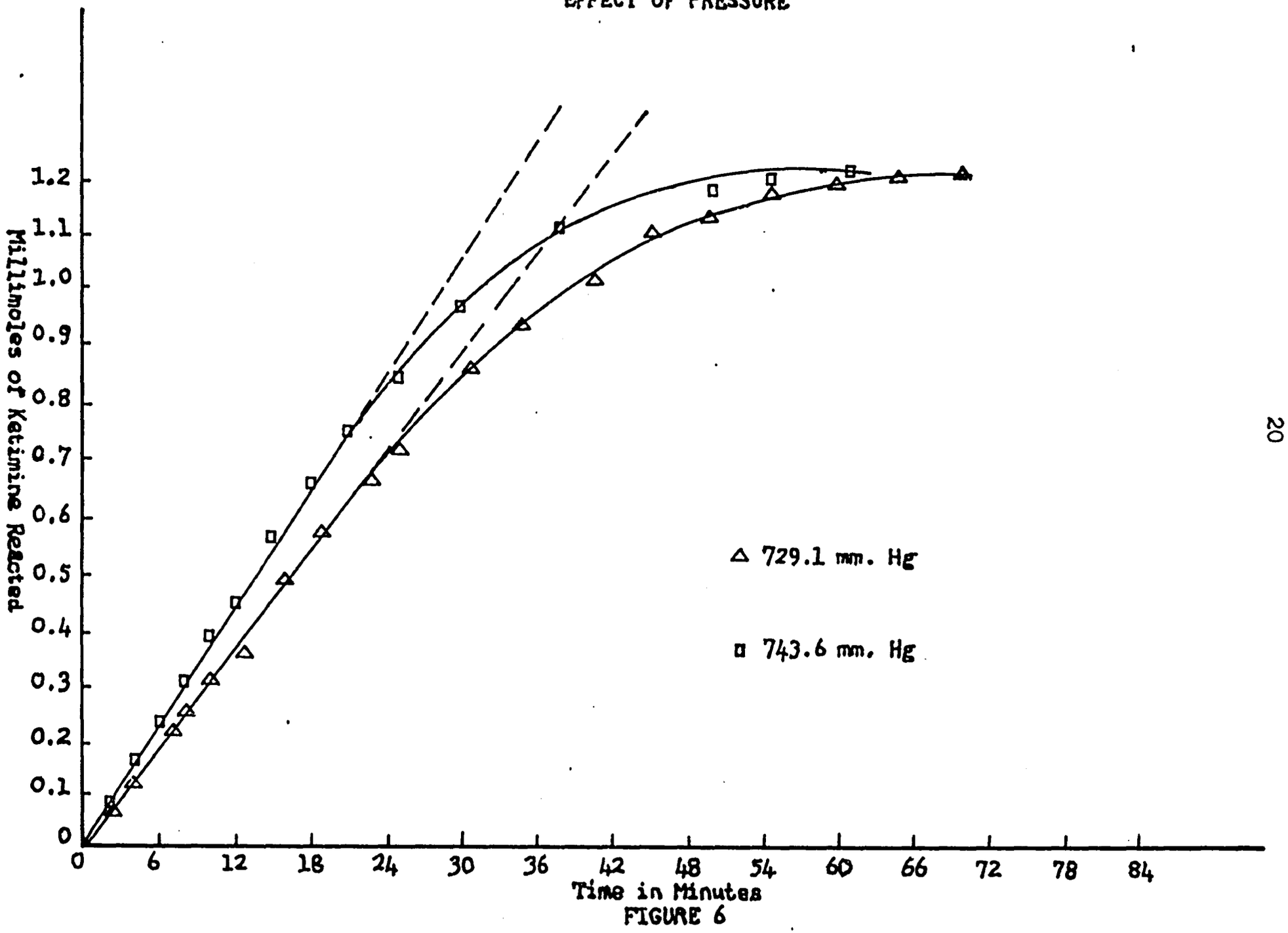

FIGURE 6

TEMPERATURE EFFECT

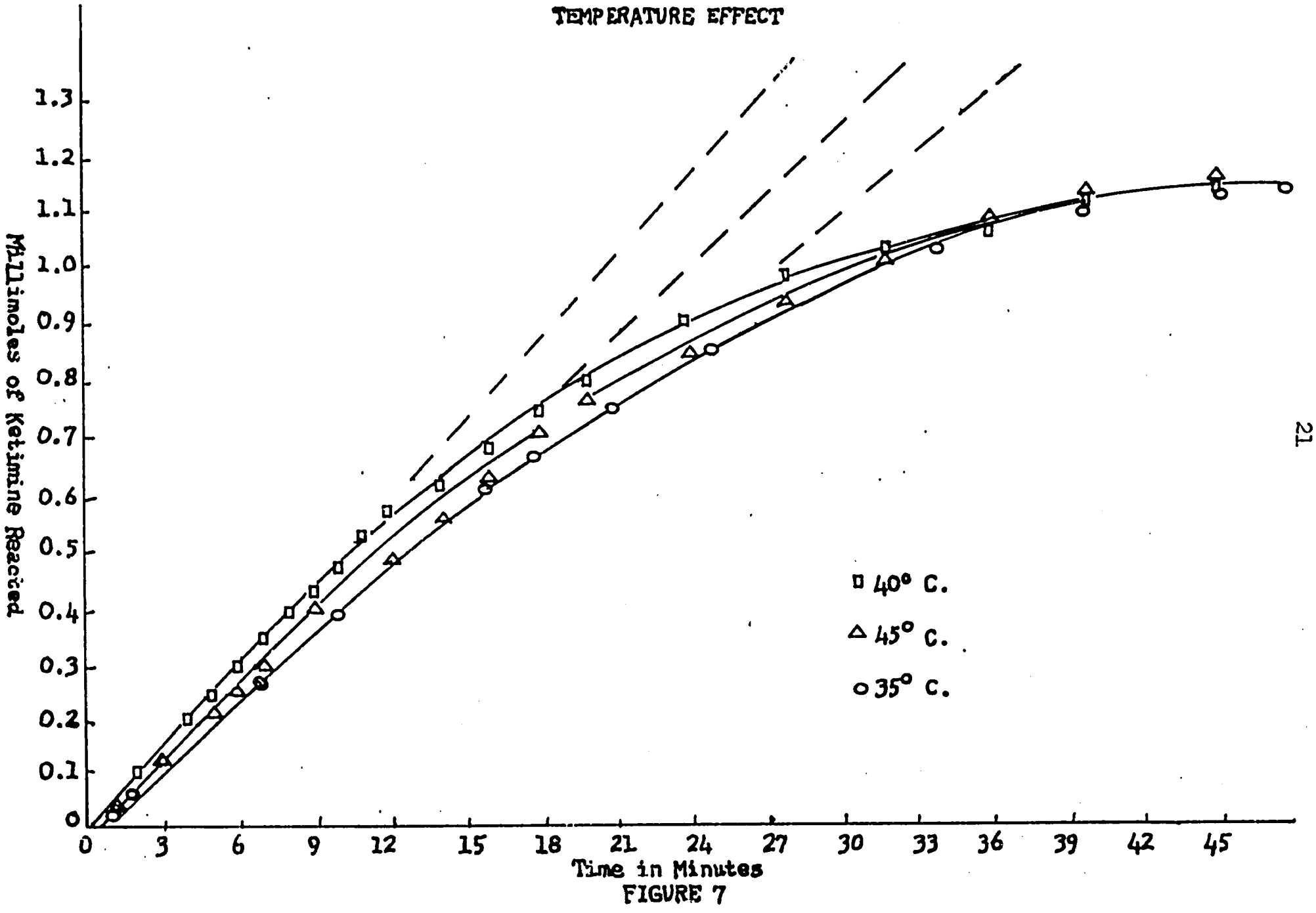

FIGURE 7

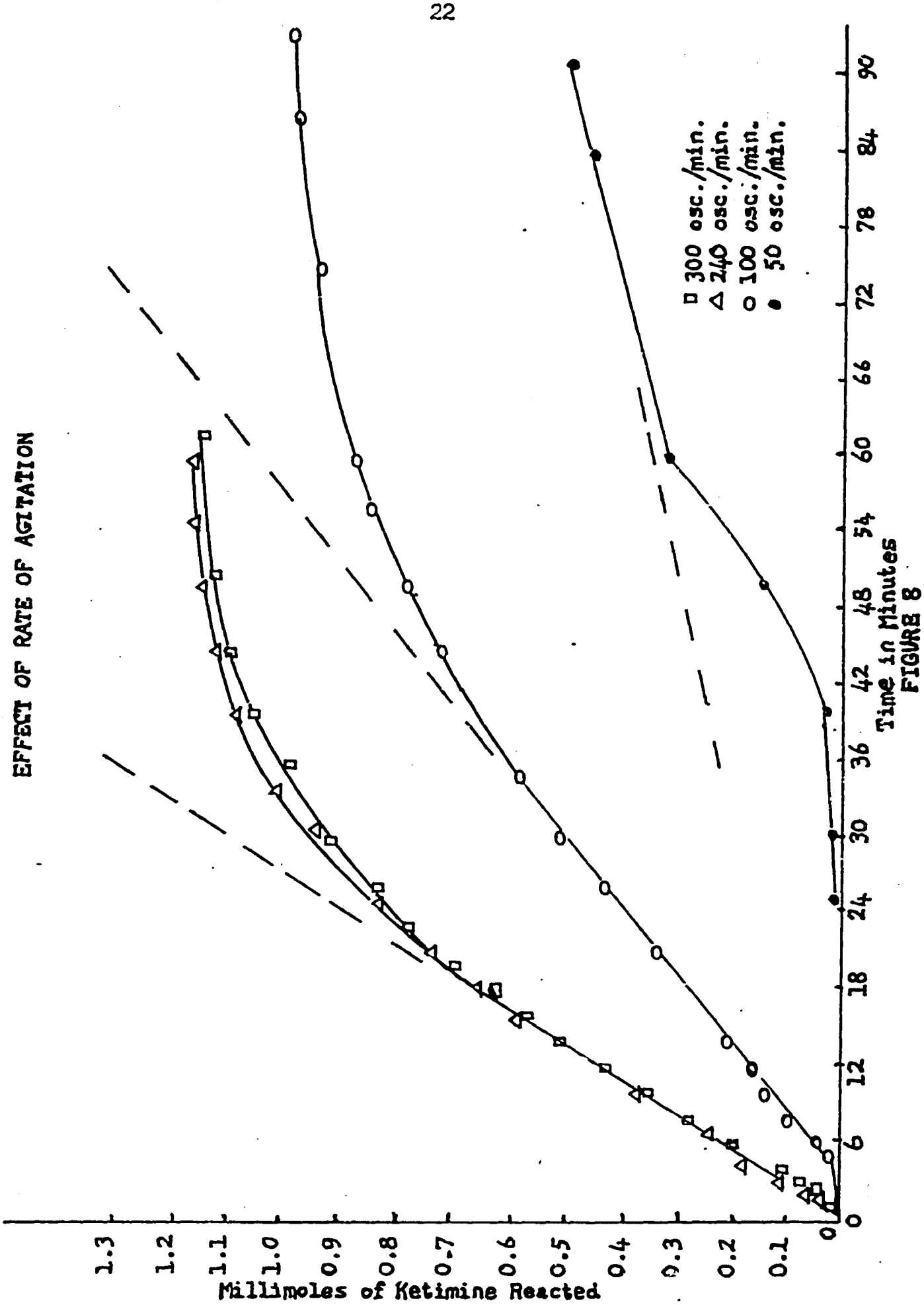
EFFECT OF RATE OF AGITATION
□ 300 osc./min.
△ 240 osc./min.
○ 100 osc./min.
● 50 osc./min.
Millimoles of Ketimine Reacted
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
6
12
18
24
30
36
42
48
54
60
66
72
78
84
90
Time in Minutes

FIGURE 8

Adsorption Isotherms of Diphenyl Ketimine and Benzhydryl Amine on PS 14 Catalyst. The adsorption isotherms of diphenyl ketimine, and its reduction product, benzhydryl amine were determined at 35 ± 0.2°C. Approximately 25 mg. of PS 14 catalyst, weighed to the closest 0.1 mg., was put into the hydrogenation flask with a measured amount of ethanol. The volume of ethanol varied from 1-9 ml. The catalyst was hydrogenated as it was in the hydrogenation rate experiments. At the end of the hydrogenation period, stopcock(6) was opened to allow the pressure within the apparatus to fall to atmospheric, then was closed. Shaking was continued for about 10 minutes to allow the system to approach equilibrium at the new pressure.

The hydrogenation flask was opened, and enough 0.2480 M ketimine or 0.2572 M amine solution was added to bring the total volume to 10 ml. The flask was then closed, shaken at 240 osc/min. for 30 minutes, and then allowed to stand for 20 minutes to allow catalyst particles to settle. At the end of this time, two one ml. samples were withdrawn and titrated with 0.01688 N $HClO_4$ in glacial acetic acid using crystal violet as indicator, as reported by Iddings[56]. The color changed for this indicator is from purple, to blue at the end point, to green in the presence of excess $HClO_4$. The color at the end point was visually compared with the color of a standard previously prepared by Iddings.

The amount of imine or amine adsorbed per gram of catalyst was computed from the titration data, corrected for the amount of solvent lost on evacuation. The amount of solvent lost on evacuation was determined as described below. The adsorption isotherms so obtained are shown in Figure 10.

HYDROGENATION OF MALEIC ACID

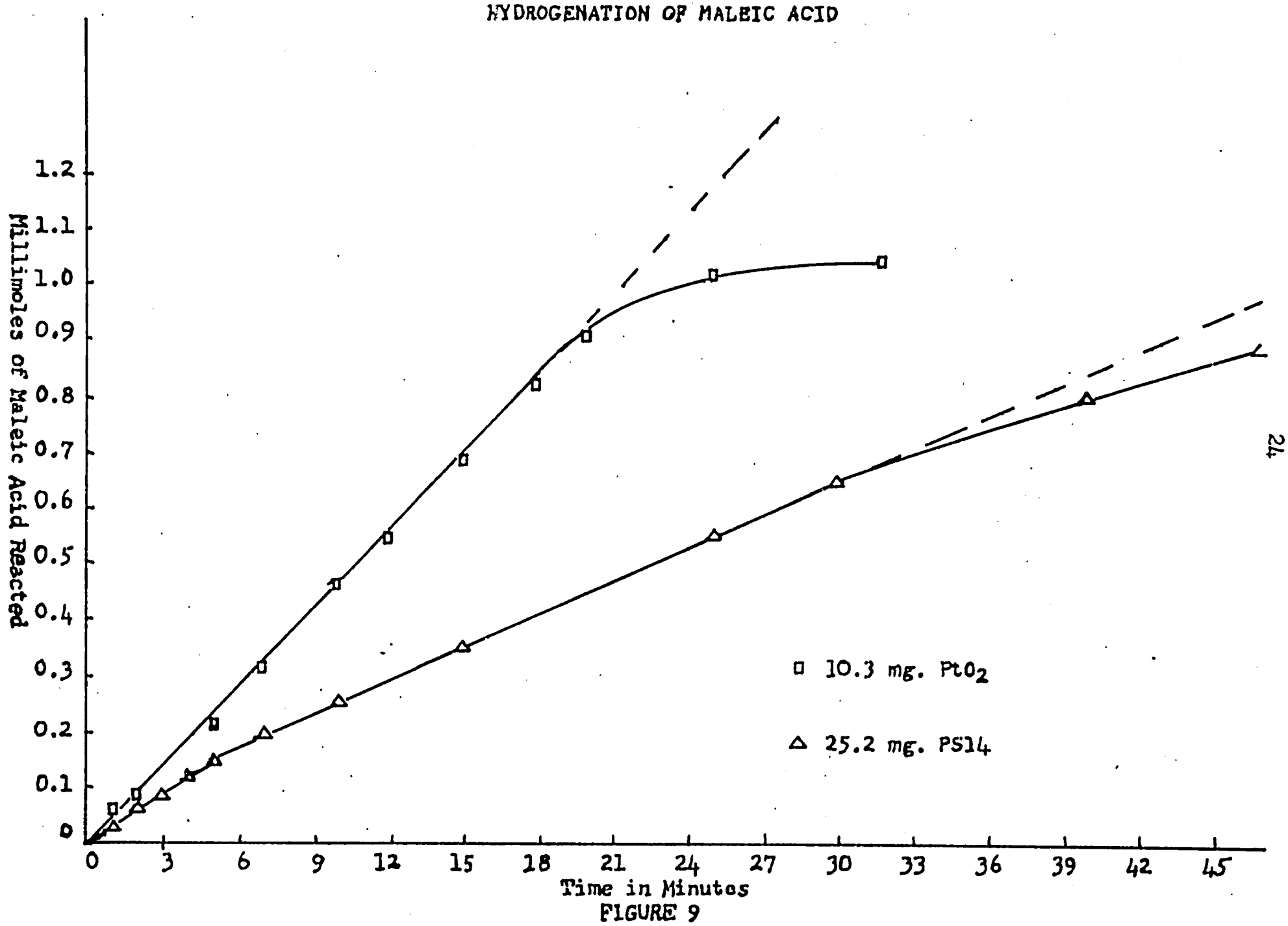

FIGURE 9

Determination of Total Volume of Solution for Adsorption Isotherm Experiments. Some ethanol was lost during evacuation of the flask prior to hydrogenation of catalyst. Since an aliquot portion of the solution remaining after adsorption was titrated, it was desirable to know the total volume of solution. This was determined by proceeding exactly as in the determination of the adsorption isotherm, but adding no catalyst. A five ml. sample of ethanol was added to the flask. The flask was then evacuated and refilled with hydrogen three times as previously described. After shaking for 30 minutes, the flask was opened, and five ml. of diphenyl ketimine solution added. This mixture was shaken for 30 minutes. Then two one ml. samples were removed and titrated. This indicated that the total volume of solution was 9.355 ml.

ADSORPTION ISOTHERMS

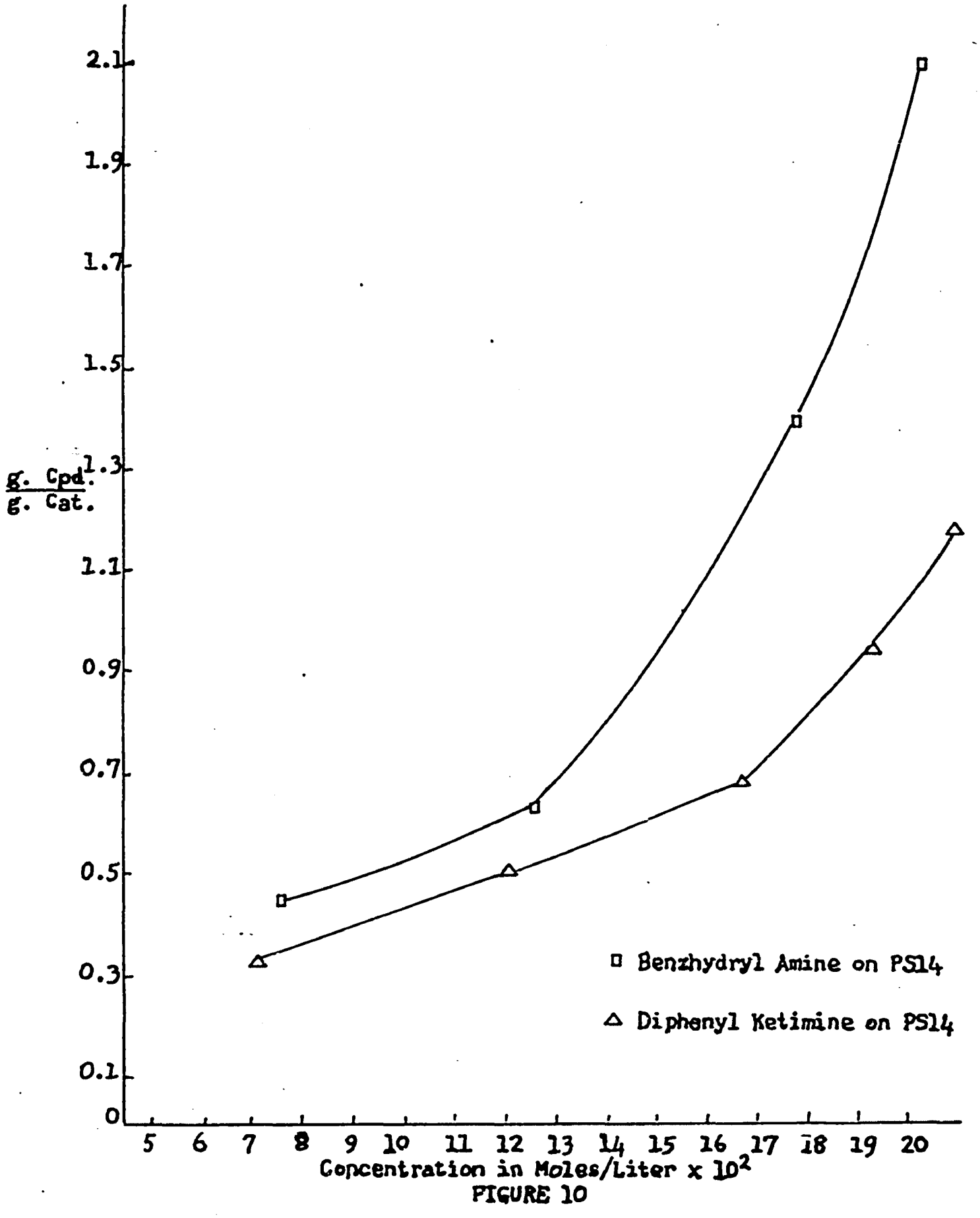

FIGURE 10

TABLE I

HYDROGENATION DATA

Figure	Millimoles[b] Of Imine	mg. Catalyst	Pressure mm. Hg	Agitation Rate osc/min.	Zero Order[a] Rate Constant
2	1.248	5.0 PS 14	745.5	240	0.98
2	1.248	10.7 PS 14	746.1	240	1.66
3,4,5, 7, 8	1.248	25.3 PS 14	735.3	240	1.37
2	1.248	28.7 PS 14	743.3	240	1.47
2	1.248	38.6 PS 14	736.2	240	1.47
2	1.248	51.5 PS 14	747.4	240	1.53
8	1.248	25.3 PS 14	740.7	50	0.30
8	1.248	25.0 PS 14	741.0	100	0.72
8	1.248	25.0 PS 14	740.9	300	1.38
7[c]	1.248	25.2 PS 14	741.5	240	1.89
7[d]	1.248	25.2 PS 14	741.5	240	1.59
3	0.482	25.5 PS 14	745.2	240	1.37
3	1.962	25.5 PS 14	745.1	240	1.37
5[e]	1.248	25.1 PS 14	734.2	240	0.94
4[f]	1.248	25.3 PS 14	741.2	240	2.29
6	1.248	10.3 PtO_2	729.1	240	2.81
6	1.248	10.3 PtO_2	743.6	240	3.41

a. Rate constants have units of millimoles ketimine/minute/gram of catalyst.
b. Temperature on all runs not otherwise indicated was 35°C.
c. Temperature 40°C.
d. Temperature 45°C.
e. 1.248 millimoles of benzhydryl amine added.
f. 5 ml. glacial acetic acid used as solvent.

CHAPTER III

DISCUSSION OF RESULTS

Vandenheuvel's PS 14 catalyst[51] was used for most of the hydrogenations herein reported. A batch of this catalyst was reported by Vandenheuvel to have given reproducible results on hydrogenation rate studies over a period of two years. Because PS 14 contains only 14% platinum by weight, somewhat larger amounts of it are necessary than is the case with Adams catalyst. This results in greater accuracy of weighing, particularly if small samples are to be hydrogenated. Weight for weight of platinum, PS 14 is claimed to be about 2.5 times as active as Adam's catalyst.

Taken as a standard for hydrogenation rate studies of diphenyl ketimine was the following set of conditions: five ml. of 0.2408 M diphenyl ketimine solution in a total volume of 10 ml. of absolute ethanol; 25 mg. of PS 14 catalyst; 240 osc/min. agitation; 35°C and a pressure of about 740 mm. The initial amount of imine, the amount of catalyst, agitation rate and temperature were successively varied, with all the other variables kept constant. The effect of using glacial acetic acid as a part of the solvent, of hydrogenating the presence of an excess of the product and the change in rate with change in atmospheric pressure were also measured. The results are shown in Figure 2-8 and tabulated in Table I.

In order to calculate the number of millimoles of hydrogen adsorbed at a particular time interval, it was necessary to make an assumption as to the pressure due to the liquid within the system. Absolute ethanol was the solvent in the reaction flask, 95% ethanol was confining fluid. Both liquids were saturated with hydrogen. The vapor pressure of the liquids within the system was arbitrarily taken as that of pure ethanol at the particular temperature[55].

The rate of liquid phase catalytic hydrogenations should depend on the temperature, and on the amount of hydrogen acceptor and hydrogen adsorbed by the catalyst. Rates of catalytic hydrogenations in general increase with increasing temperature. The total amount of hydrogen adsorbed should depend primarily on the pressure and on the amount of catalyst. The amount of hydrogen acceptor adsorbed may vary with the temperature, concentration of hydrogen acceptor in the liquid phase, amount of catalyst and, in the case of nitrogen compounds, may vary greatly with the type of solvent. Ketimines, for example, would be expected to be a great deal more strongly adsorbed than the corresponding ketiminium ion[57].

Figure 8 shows the effect of agitation rate on the hydrogenation of diphenyl ketimine. It should be noted that the runs at 50 and 100 osc/min. show a lag initially. This is believed to be due to slow establishment of adsorption equilibrium of diphenyl ketimine, since the catalyst was prehydrogenated. At shaking rates of 240 osc/min. or higher, the equilibrium is apparently rapidly established, since no lag is noted. No data are included on hydrogenations carried out with magnetic stirring because it was noted that the catalyst stuck to the plastic covered stir-

ring bars, and glass covered stirring bars were too fragile.

The distinguishing characteristic of a zero order reaction, that the initial concentration of the reactant has no effect on the rate of the reaction, is shown in Figure 3. Also indicated is the fact that adsorption equilibrium of diphenyl ketimine is apparently as rapidly established in dilute solutions as in concentrated.

The effect of an increase in pressure is shown in Figure 6. For a 14.5 mm. pressure change, the rate constant changes from 2.81 to 3.41.

Rather curious behavior may be noted in Figure 7. As the temperature was increased from 35°C an increase in the rate constant is noted followed by a decrease at 45°C. Two opposing factors are probably in operation. The speed of the reaction between hydrogen and the imine is increased at increasing temperatures, while the amount of imine and possibly also of hydrogen adsorbed by the catalyst should be decreased[58]. Apparently the decrease in adsorption outstrips the increase in reaction speed.

Somewhat inconsistent results are shown in Figure 2. But for the run with 10.7 mg. of catalyst, the rate constants enumerated in Table I are seen to increase when calculated in a gram basis. Zero order rate constants taken directly from the slopes of the curves increase steadily from 0.0048 millimoles Imine/minute for 5 mg. catalyst to 0.078 millimoles Imine/minute for 51.5 mg. catalyst. The inconsistency might be partially explained by the fact that the 10.7 mg. hydrogenation was carried out at somewhat higher pressure than the remainder of this particular series of runs. It should be noted also that as higher amounts of catalyst are used, the reaction becomes more nearly zero order throughout. This

indicates that with smaller amounts of catalyst, the product is able to occupy a fairly large proportion of the surface of the catalyst, and thus inhibit the reaction of hydrogen and imine to some extent. This would require that the product, benzhydryl amine, be more strongly adsorbed than the ketimine. That this is the case may be seen in Figure 10. In determination of the adsorption isotherm of diphenyl ketimine on the previously hydrogenated catalyst, it is realized that some hydrogenation to the amine occurs. However, since the determination of the adsorption isotherm was carried out at atmospheric pressure in the absence of an excess of hydrogen, the amount of the imine hydrogenated is believed to be small. Even if it were hydrogenated to a considerable extent, this would make the actual adsorption of the imine smaller yet. Both the isotherms indicate van der Waals or physical adsorption, and are of type III as designated by Brunaer et al[59]. This type of isotherm indicates that the heat of vaporization of the adsorbate is greater than the heat of formation of the first layer of adsorbate on the catalyst. Thus multilayers of the adsorbate are built up.

The fact that the presence of an initial excess of amine actually retards the reaction is shown in Figure 5.

Since the positive ions formed by both the imine and the amine would be expected to be less strongly adsorbed than the imine and amine themselves, acetic acid was added as part of the solvent. The results are shown in Figure 4. Apparently the adsorption of the imine is affected less by the presence of acid than is that of the amine, because of a marked increase in rate.

The results obtained, particularly the adsorption isotherms,

lead to the conclusion that the hydrogenation of diphenyl ketimine takes place by a Rideal-Eley mechanism[3], with hydrogen chemically adsorbed by the catalyst, and the diphenyl ketimine in a van der Waals layer. The reaction is inhibited by the preferential adsorption of benzhydryl amine to that of diphenyl ketimine, which reduces the amount of catalyst surface available to the reactants.

Figure 10 shows data for the hydrogenation of maleic acid by the PtO_2 and PS 14 catalysts used in this work. The rate constants calculated from the slopes of the curves are 0.84 millimoles maleic acid/minute/g. PS 14 and 3.50 millimoles H_2/minute/g. PtO_2. In both cases 1.196 millimoles of maleic acid were hydrogenated in a total volume of 10 ml. of absolute ethanol, 35°C was the temperature and the agitation rate was 240 osc/min. For PS 14, the amount of catalyst used was 25.0 mg. and the pressure was 741.9 mm. For PtO_2, the amount used was 14.0 mg. and the pressure was 747.1 mm. Assuming the PS 14 to contain 14% Pt, the rates per gram of Pt would be 6.0 for PS 14 and 4.42 for the PtO_2. The rate for PtO_2 was measured at a somewhat higher pressure than the rate using PS 14, which may account for the lower relative rates than noted by Vandenheuvel.

CHAPTER IV

SUMMARY

In order to establish a set of conditions for hydrogenation rate studies of ketimines, the hydrogenation of diphenyl ketimine was rather exhaustively studied. These studies were carried out in apparatus similar to that suggested by Vandenheuvel[54].

An ethanol solution of diphenyl ketimine was hydrogenated with Vandenheuvel's PS 14 catalyst[51], and with Adam's PtO_2 catalyst[49]. Vandenheuvel's catalyst should be an important adjunct to kinetic studies because of its relatively high activity (2.5 times as active as Adam's catalyst per weight of Pt), and because of the fact that its activity changes very slightly with age.

The standard hydrogenation rate experiment used in this work was; 1.248 millimoles of diphenyl ketimine in 10 ml. of absolute ethanol, 25 mg. of PS 14 catalyst, 35°C, 240 osc/min. agitation and about 740 mm. pressure. The concentration of ketimine, amount of catalyst, temperature and agitation rate were successively varied, with all the other factors kept constant.

The rate of hydrogenation of diphenyl ketimine was found to be independent of the initial concentration of ketimine, and independent of the agitation speed above 240 osc/min.

An increase in pressure was found to increase the reduction rate. Upon an increase in the amount of catalyst, the rates were found to increase, but not in proportion to the amount of catalyst added. The reduction rate at 45°C was found to be intermediate between those at 35° and 40°C, the 40°C rate being the greatest.

At low agitation rates, a lag was noted in the initial part of the reaction. This was ascribed to the slow establishment of adsorption equilibrium.

The rate constant was found to be increased by use of acetic acid as solvent, and decreased by the presence of an excess of the product, benzhydryl amine.

The reduction of diphenyl ketimine under the above conditions is a zero order reaction initially, but is inhibited by the product. From the data available including adsorption isotherms of diphenyl ketimine and benzhydryl amine, it is concluded that the reduction of diphenyl ketimine takes place by a Rideal-Eley mechanism.

Data on the hydrogenation of maleic acid by the two catalysts used indicates that the PS 14 catalyst was at least 1.35 times as active per weight of Pt as the Adams catalyst used.

It is recommended that future studies on the hydrogenation of ketimines be carried out in the following manner: PS 14 catalyst is recommended, agitation rates of about 240 osc/min. should be adequate, a temperature of about 35°C, and pressure atmospheric, or, slightly above. Temperature and pressure must be accurately controlled. It is also recommended that adsorption isotherms for the ketimine and its reduction product be determined.

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